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| <b>(54) Title:</b> GRANULATE DETERGENT ENZYME PRODUCT, METHOD FOR PRODUCTION THEREOF, USE<br>THEREOF, AND DETERGENT CONTAINING SUCH PRODUCT<br><br><b>(57) Abstract</b><br><br>The granulate detergent enzyme product comprises a core of an enzyme containing material with a coating contain-<br>ing a mono- and/or diglyceride of a fatty acid, with a content of monoglyceride in relation to the total amount of mono-<br>and diglyceride of at least 30 % by weight and preferably with a melting point above 35°C. Due to the coating the enzymat-<br>ic stability is enhanced, in the presence of other detergent components, especially strong bleaching agents. The coating is<br>usually carried out in a rotating mixer. Also coatings with antioxidants enhance the enzymatic stability. |           |  |

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GRANULATE DETERGENT ENZYME PRODUCT, METHOD FOR PRODUCTION  
THEREOF, USE THEREOF, AND DETERGENT CONTAINING SUCH  
PRODUCT

5

#### TECHNICAL FIELD

The technical field to which this invention  
pertains comprises a granulate detergent enzyme product  
10 comprising a core of a microbial enzyme containing  
material and a coating, a method for production of such  
product, a use of such product, and a detergent or a  
detergent component containing such product.

15

#### BACKGROUND ART

The field of enzymatic detergent additives has  
been rapidly growing during the last decades. Reference is  
20 made to e.g. the article "How Enzymes Got into  
Detergents", vol. 12, Developments in Industrial  
Microbiology, a publication of the Society for Industrial  
Microbiology, American Institute of Biological Sciences,  
Washington, D.C. 1971, by Claus Dambmann, Poul Holm, Villy  
25 Jensen and Mogens Hilmer Nielsen, to the article  
"Production of Microbial Enzymes", Microbial Technology,  
Sec. ed., Vol. I, Academic Press, 1979, pages 281 - 311,  
by Knud Aunstrup, Otto Andresen, Edvard A. Falch and Tage  
Kjaer Nielsen, and to P.N. Christensen, K. Thomsen and S.  
30 Branner: "Development of Detergent Enzymes", a paper  
presented on 9 October 1986 at the 2nd World Conference on  
Detergents held in Montreux, Switzerland.

The commonest enzymatic detergent additive is a  
proteolytic additive, but also amylolytic, cellulolytic,  
35 and lipolytic detergent additives are described, e.g. in  
GB patent No. 1 554 482, BE patent No. 888 632, and US  
patent No. 4,011,169, column 4, line 65 to column 5, line

68. The above list of enzymes is not exhaustive, but represents the commonest enzymatic additives used in detergents.

Enzymatic detergent additives for use in powder  
5 detergents are usually prepared in the form of dust-free granulates. These granulates can be produced in several different ways. Reference can be made to GB patent No. 1 362 365 which describes the production of enzyme containing granulates used as detergent additives by means  
10 of an apparatus comprising an extruder and a spheronizer (sold as MARUMERIZER®), and to US patent No. 4 106 991, which describes the production of enzyme containing granulates used as detergent additives by means of a drum granulator. Reference is also made to European patent  
15 publication EP-A-0170360 which describes enzyme granulates containing certain salts to improve the storage stability.

Whereas enzyme granulates prepared according to known methods are entirely satisfactory for use in many commercial powder detergents, we have recognized that  
20 enzyme stability of these granulates is reduced in certain detergent formulations and at certain storage conditions. These include particularly detergents with high water content and/or high pH and/or high content of bleaching agents and particularly storage at high humidity and  
25 temperature.

Thus, we have recognized that a need exists for a particulate detergent enzyme product which is modified in such manner that the enzymatic stability is improved considerably in adverse detergent formulations and/or at  
30 adverse storage conditions, whereby this modification in no regard should impair any process or material related to the continued storage and later use of the product.

## DISCLOSURE OF INVENTION

After considerable research on new coatings we have surprisingly discovered that a coating of the  
5 particulate detergent enzyme with only one specified category of coating agents, out of many possibilities, will modify the particulate detergent enzyme in the wanted manner, i.e. this coating will improve the enzymatic stability at adverse conditions, without any accompanying  
10 unwanted side effects.

Thus, the granulate detergent enzyme product according to the invention comprises a core of a microbial enzyme-containing material and a coating thereon, wherein the coating comprises a coating agent, which is a mono-  
15 and/or diglyceride of a fatty acid.

It goes without saying that the coating agent comprising a mono- and/or diglyceride of a fatty acid should be solid at any normal use temperature of the product according to the invention. Also, the coating  
20 agent may be a single mono- and/or diester of a fatty acid or a mixture of such esters.

In this specification with claims the detergent concept is to be understood in a broad sense. Thus, the term granulate detergent enzyme product is intended to  
25 include any granulate enzyme product which is a part of or is intended later to be a part of any cleaning or cleansing composition, e.g. a heavy duty detergent, a dish washing agent, a bleaching agent, a softener, a color clarification agent or a pure surfactant. Further, the  
30 detergent according to the invention comprises any cleaning or cleansing composition containing the product according to the invention, and the detergent component according to the invention comprises for instance a bleaching agent, a softener, a color clarification agent  
35 or a pure surfactant containing the product according to the invention.

The invention is mainly concerned with microbially produced enzymes, as other enzymes usually are not suited as enzymatic detergent additives, mainly due to cost and stability considerations.

5           Thus, the product according to the invention possesses the above indicated coating on a core. However, the product according to the invention may also comprise a precoating of another coating agent on the core and/or a subsequently applied coating with another coating agent on  
10 the coating of the invention. Such other coating agents may for instance be the coating agents described in DK patent application no. 121/88.

          The coating agent does not generate any disturbing influence during the washing process, as it  
15 will emulsify in the washing liquid, whereafter the enzyme can exert its wanted activity on the laundry. Also, especially in a damp atmosphere and at relatively high temperatures it has been found that the enzymatic stability is satisfactory during storage of the product  
20 according to the invention in the presence of powerful bleaching agents.

          From DK patent application nos. 121/88 and 612/88 it appears that coating of a particulate detergent enzyme with an enteric coating agent will improve the  
25 enzymatic stability in the presence of powerful bleaching agents; even if this coating agent provides a good stability increase in the presence of powerful bleaching agents, the prior art coating is open to improvement, and surprisingly it has been found that the enzyme stability  
30 in the presence of powerful bleaching agents of the detergent enzyme product according to the invention is considerably better than the enzyme stability in the presence of powerful bleaching agents of the prior art detergent enzyme product.

35           Also, it appears from publications from Grindstedværket, Grindsted, Denmark, e.g. Grindsted Products, Grindsted Emulsifiers and Stabilizers for Food

(GB5-4e) that the coating agent used according to the invention is produced and used as an emulsifier and stabilizer in the food industry. However, the use of these glycerides as coating agents in order to stabilize enzyme activity in an aggressive environment generated by other detergent components is not described in these publications or made obvious on the basis thereof.

In a preferred embodiment of the product according to the invention the melting point of the coating agent is above 35°C, preferably above 50°C. In this manner ordinarily no melting problems will occur, even in tropical regions.

In a preferred embodiment of the product according to the invention more than 90% of the enzyme granulate cores exhibit particle sized between 2 and 3000 µm. This particle size interval covers practically all commercially used detergents.

In a preferred embodiment of the product according to the invention more than 90% of the enzyme granulate cores exhibit particle sizes between 100 and 400 µm. This so-called microgranulate corresponds to a commercially available detergent.

In a preferred embodiment of the product according to the invention more than 90% of the enzyme granulate cores exhibit particle sizes between 250 and 1200 µm. This so-called standard granulate corresponds to usual commercially available detergents.

In a preferred embodiment of the product according to the invention the weight of the coating is between 0.1 and 100% by weight of the core. If the weight of the coating is less than 0.1%, no satisfactory effect will be obtained, and if the weight of the coating is above 100%, the product will be too expensive, and also, no further stabilizing effect will be obtained.

In a preferred embodiment of the product according to the invention the weight of the coating is between 1 and 30% by weight of the core, preferably

between 2 and 20% by weight of the core. These intervals represent advantageous compromises between economy and satisfactory performance.

In a preferred embodiment of the product  
5 according to the invention the main fatty acid(s) of the coating agent is/are palmitic and/or stearic acid. These glycerol esters are available on the market and exhibit an excellent stabilizing effect.

In a preferred embodiment of the product  
10 according to the invention the coating contains between 10 and 100% of the coating agent (on a dry substance basis). If the coating contains less than 10% of the coating agent, the impermeability of the coating is usually not satisfactory.

15 In a preferred embodiment of the product according to the invention the part of the coating which is not the glyceride coating agent is a filler, which can be any salt, preferably  $\text{CaCO}_3$ ; talc, silica and/or  $\text{TiO}_2$ . The filler may be added for economic and/or cosmetic  
20 purposes. The coating can consist of coating agent entirely, and also, other additives than fillers may be present in the coating.

In a preferred embodiment of the product according to the invention the enzyme is one or more of a  
25 protease, an amylase, a lipase, a cellulase, and an oxidase. These are the most commonly used detergent enzymes. Practice of the invention applies to any detergent enzyme.

In a preferred embodiment of the product  
30 according to the invention the particles of enzyme containing material are commercially available granulates. These granulates may already be coated, but their coating does not generate a satisfactory enzyme stability in the presence of powerful bleaching agents. Such particles are  
35 easily available and are well suited for the invention.



In a preferred embodiment of the product according to the invention the particles already possess or are given a coating containing or consisting of an antioxidant, preferably as an undercoat to the coating.

5 This embodiment is specially well suited in such cases in which the granulate detergent enzyme product is mixed with a powerful bleaching agent. In that case small amounts of humidity saturated with bleaching agent may diffuse into the enzyme granules, even through the coating, and impair  
10 the stability of the enzyme. In this embodiment, however, the antioxidant in the undercoat will react with the bleaching agent and thus improve the enzyme stability. The antioxidant may be a thiosulphate, preferably ammonium or sodium thiosulphate, a sulfite, a bisulfite, an ascorbic  
15 acid or a salt of ascorbic acid.

Furthermore, the invention comprises a method for production of the product according to the invention, wherein the cores are introduced into a rotating mixer and heated to a temperature above 35°C, whereafter melted  
20 coating agent is added, and the product is removed from the rotating mixer when equilibrium is obtained. This method is cheap, dependable and well suited for large scale production.

Also, the invention comprises a method for  
25 production of the product according to the invention, wherein the cores are suspended in melted coating agent and the thus formed mixture is introduced on the surface of a fast spinning, horizontal wheel, whereafter the product is collected downstream the spinning wheel. By  
30 means of this method a very homogenous product is obtained. The general principle of this method is described in the International patent application no. PCT/US85/00827.

Also, the invention comprises a method for  
35 production of the product according to the invention, wherein the cores are suspended in a solution of the coating agent in an organic solvent, whereafter the

suspension is introduced into a fluid bed dryer and the product is collected. This method is especially well suited for laboratory experiments and pilot plant runs.

Also, the invention comprises a use of the  
5 granulate detergent enzyme product according to the invention as a constituent of a detergent or of a detergent component.

In a preferred embodiment of the use according to the invention the detergent or the detergent component  
10 appear as a slurry. In this manner a physically stable mixture can easily be obtained by addition of sedimentation inhibition agents.

In a preferred embodiment of the use according to the invention the detergent or the detergent component  
15 appear as a particulate material. In this manner it is possible to obtain a mixture, the homogeneity of which does not change with time.

In a preferred embodiment of the use according to the invention the detergent component is a bleaching  
20 agent. It has been found that the stability of the product is satisfactory even in the presence of powerful bleaching agents.

Finally the invention comprises a detergent or a detergent component, containing as a constituent the  
25 product according to the invention.

In a preferred embodiment of the detergent or detergent component according to the invention the detergent component appear as a slurry. In this manner a physically stable mixture can easily be obtained by  
30 addition of sedimentation inhibition agents.

In a preferred embodiment of the detergent or detergent component according to the invention the detergent or the detergent component appear as a particulate material. In this manner it is possible to  
35 obtain a mixture, the homogeneity of which does not change with time.

In a preferred embodiment of the detergent or detergent component according to the invention the detergent component appear as a particulate material, and the detergent component contains a bleaching agent. It has  
5 been found that the stability of the product is satisfactory even in the presence of powerful bleaching agents.

In a preferred embodiment of the detergent component according to the invention the detergent  
10 component appear as a particulate material, the detergent component contains a bleaching agent, and the bleaching agent is coated with a sustained release coating agent, preferably a sustained release coating agent containing montmorillonite, as described in patent application DK  
15 1378/88, filed on the same date as this application. It has been found that the stability of the product is excellent even in the presence of powerful bleaching agents.

The invention will be illustrated by means of  
20 the following examples. In all examples comprising proteolytic enzymes containing granulates the proteolytic enzyme containing granulates are produced according to example 1 in US patent No. 4,106,991, except that a sulphate based formulation is used instead of a chloride  
25 based formulation.

#### EXAMPLE 1

30 This example describes a method for production of the granulate detergent enzyme product according to the invention.

7 kg of sodium sulphate based ALCALASE® granulate of 2.6 Anson units/g and with a particle size of  
35 300 - 1000  $\mu\text{m}$  is heated in a Lödige mixer M20 to approximately 70°C. ALCALASE is a trademark for a Bacillus licheniformis proteinase, owned by Novo Industri A/S, Novo

Allé, 2880 Bagsværd, Denmark. Then 350 g (5%) of melted Grindtek MSP 90 is added to the mixer and distributed on the surface of the ALCALASE granulate by mixing for 5 minutes. Grindtek MSP 90 is a mixture of around 90% of 5 monoglyceride of palmitic acid and stearic acid and around 10% of diglyceride of palmitic acid and stearic acid. A powder mixture of titanium dioxide and magnesium silicate (700 g) is added as a colouring agent. The powder is worked into the melted wax by mixing for 10 minutes. 10 Finally 140 g (2%) of melted Grindtek MSP 90 is added. After mixing for 3 minutes the granulate will be non dusting. A product with a tight coating with a shell of Grindtek MSP 90 has been obtained.

15

**EXAMPLE 2**

7 kg of SAVINASE granulate of an activity which after coating generates an activity of 6.0 KNPu/g is 20 coated as described in example 1 with Grindtek MM90 (glyceryl myristate) Grindtek ML90 (glyceryl laurate) and Grindtek MSP90 (glyceryl stearate/palmitate), respectively. As a prior art reference, coating is performed with PEG 4000. In contradistinction to example 1 25 a 2:1 mixture of titanium dioxide:kaolin is used as a colouring agent in example 2.

Storage stability for preparations according to example 2.

Storage conditions: Powder detergent with 25% 30 perborate, 37°C, 70% relative humidity, open glasses.

|    | Coating      | Colouring agent | % Residual activity |               |                |
|----|--------------|-----------------|---------------------|---------------|----------------|
|    |              |                 | <u>3 days</u>       | <u>7 days</u> | <u>14 days</u> |
| 5  |              |                 |                     |               |                |
| A  | 6.4% MM90    | 12.5%           | 83-86               | 44-43         | 26-25          |
| B  | 6.9% ML90    | 12.5%           | 82-83               | 43-44         | 28-27          |
| C  | 7.0% MSP90   | 12.5%           | 79-79               | 41-41         | 23-24          |
| E* | 7.0% PEG4000 | 12.5%           | 67-68               | 27-31         | 18-18          |

10

\* Preparation E prior art

All calculations of amounts are based on uncoated granulate.

15

### EXAMPLE 3

Preparations A, B, C, and E: 7 kg of ALCALASE  
 20 granulate (2.8 Anson Units/g) is coated as described in  
 example 1 with Grindtek MSP40 (A), Grindtek MSP90 (B),  
 Grindtek MSP90/bisulfite (C, titanium dioxide/Mg-silicate  
 is mixed with finely ground Na-bisulfite corresponding to  
 4%, calculation based on uncoated granulate). Sample E is  
 25 coated with PEG4000 corresponding to prior art.

Preparation D: This preparation is prepared with  
 an extraordinary thick coating with MSP90, as follows: 7  
 kg of ALCALASE granulate (2.8 Anson units/g) is  
 alternately sprayed with MSP90 and powdered with pure  
 30 kaolin (type Speswhite/EEC) in such manner that there was  
 never any significant excess of either MSP90 or kaolin.  
 Totally 1.3 kg of MSP90 (18.6%) and 5.0 kg of kaolin  
 (71.4%) is applied calculated on uncoated granulate.

Storage conditions: Powder detergent with 25%  
 35 perborate, 37°C, 70% relative humidity, open glasses.

|       | <u>Coating</u> | <u>Colouring agent</u> | <u>% Residual activity</u> |               |                |
|-------|----------------|------------------------|----------------------------|---------------|----------------|
|       |                |                        | <u>3 days</u>              | <u>7 days</u> | <u>14 days</u> |
| 5     |                |                        |                            |               |                |
| A     | 6.6% MSP40     | 12.5%                  | 92-90                      | 48-53         | 22-19          |
| B     | 7.0% MSP90     | 11.3%                  | 90-91                      | 44-43         | 23-26          |
| 10 C  | 9.0% MSP90     | 11.3%                  | 93-96                      | 59-58         | 30-33          |
|       |                | 4% bisulfite           |                            |               |                |
| D     | 18.6% 20 MSP90 | 71.4% kaolin           | 98-95                      | 83-83         | 60-59          |
| 15 E* | 7.0% PEG4000   | 12.5%                  | 82-81                      | 30-31         | 19-18          |

\* Ref. Prior art

#### 20 EXAMPLE 4

Preparation A: 7.0 kg of SAVINASE granulate is coated on a fluid-bed, Glatt WSG 5, whereby a layer consisting of 350 g of ammonium thiosulphate and 350 g of  
 25 bentonite (type ASB 350 ECC) is applied with simultaneous drying. The thiosulphate/bentonite is sprayed from a solution/suspension of the indicated components in 1 kg of water. Process parameters: Temperature in/out: 50/35°C. After the coating a subsequent drying is performed.

30 Preparation B: Preparation A coated with Grindtek MSP90 and colouring agent titanium dioxide:kaolin 2:1; otherwise as example 1.

Preparation C: The prior art reference is coated with PEG4000 and colouring agent as preparation B;  
 35 otherwise according to example 1.

Storage conditions: Powder detergent with 25% perborate, 37°C, 70% relative humidity, open glasses.

| 5    | <u>Coating</u> | <u>Colouring agent</u> | <u>% Residual activity</u> |               |                |
|------|----------------|------------------------|----------------------------|---------------|----------------|
|      |                |                        | <u>3 days</u>              | <u>7 days</u> | <u>14 days</u> |
| 10 A |                |                        | 89-90                      | 64-60         | 30-30          |
| B    | 5% MSP90       | 12.5%                  | 101-99                     | 92-92         | 52-52          |
| C    | 7% PEG4000     | 12.5%                  | 62-65                      | 43-42         | 21-22          |

#### 15 EXAMPLE 5

Preparation A: Identical to preparation B from example 4.

Preparation B: Corresponds to preparation A, but  
20 in coating with ammonium thiosulphate a bentonite of type ASB 350S, EEC is used.

Preparation C: Corresponds to preparation A, but the bentonite in the thiosulphate coating is substituted by kaolin (Speswhite, ECC).

25 Preparation D: Coating with Grindtek MSP90 and with colouring agent titanium dioxide:kaolin; otherwise according to example 1.

Preparation E: The prior art reference of coating is performed with PEG4000 and the colouring agent  
30 titanium dioxide:kaolin; otherwise according to example 1.

Storage conditions: Powder detergent with 25% perborate, 37°C, 70% relative humidity, open glasses.

|      | <u>Coating</u> | <u>Colouring agent</u> | <u>% Residual activity</u> |               |                |
|------|----------------|------------------------|----------------------------|---------------|----------------|
|      |                |                        | <u>3 days</u>              | <u>7 days</u> | <u>14 days</u> |
| 5    |                |                        |                            |               |                |
| A    | 5% MSP90       | 12.5%                  | 100-99                     | 88-84         | 53-53          |
| B    | 5% MSP90       | 12.5%                  | 91-91                      | 74-78         | 41-41          |
| C    | 5% MSP90       | 12.5%                  | 94-93                      | 71-76         | 46-46          |
| D    | 7% MSP90       | 12.5%                  | 65-65                      | 30-30         | 16-16          |
| 10 E | 7% PEG4000     | 12.5%                  | 53-52                      | 23-23         | 15-15          |

## EXAMPLE 6

15 Preparation A: ALCALASE granulate of 2.8 Anson Units/g coated with 7.0% Grindtek MSP90 and colouring agent 12.5% 2:1 titanium dioxide:Mg-silicate according to example 1.

Preparation B: ALCALASE granulate as preparation  
20 A coated with 7% PEG4000 and colouring agent as preparation A (prior art).

Storage conditions: Powder detergent with 25% perborate, 37°C, 70% relative humidity, open glasses.

25

|    | <u>Coating</u> | <u>Colouring agent</u> | <u>% Residual activity</u> |               |                |
|----|----------------|------------------------|----------------------------|---------------|----------------|
|    |                |                        | <u>3 days</u>              | <u>7 days</u> | <u>14 days</u> |
| 30 |                |                        |                            |               |                |
| A  | 7% MSP90       | 11.3%                  | 86-85                      | 55-52         | 27-25          |
| B  | 7% PEG4000     | 11.3%                  | 71-68                      | 31-32         | 18-17          |



## EXAMPLE 7

Preparation A: Corresponds to preparation B, example 3.

5 Preparation B: Corresponds to preparation C, example 3.

Preparation C: ALCALASE granulate of 2.8 Anson Units/g coated with 7% PEG4000 and 12.5% colouring agent 4:1 titanium dioxide:Mg-silicate, whereby the colouring  
10 agent is mixed with 4% Na-bisulfite (antioxidant), calculation based on uncoated granulate. Finally, an enteric overcoating with 5% Eudragit L30D is performed according to EP-A-0 270 608 (prior art).

Preparation D: Corresponds to preparation E,  
15 example 3 (prior art).

Storage conditions: Powerful acid bleach, 30°C, 60/80% relative humidity, closed cardboard boxes.

| 20   | Coating    | Colouring agent | % Residual activity after 4 weeks of storage |         |
|------|------------|-----------------|--|---------|
|      | _____      | _____           |  |         |
| A    | 7% MSP90   | 11.3%           | 18%  | SD 0.7% |
| 25 B | 9% MSP90   | 11.3%           | 29%  | SD 2.4% |
|      |            | 4% bisulfite    |  |         |
| C    | 7% PEG4000 | 11.3%           | 14%  | SD 0.5% |
|      |            | 4% bisulfite    |  |         |
| 30   |            | 5% Eudragit     |  |         |
| D    | 7% PEG4000 | 12.5%           | 9%   | SD 0.3% |

35 Residual activity is measured by dividing the contents of the cardboard box by means of a sample divider. 4 of the divided samples have been analyzed.

**EXAMPLE 8**

Preparations as example 7.

Storage conditions: Bleach as example 7, 37°C,  
5 70% relative humidity, closed cardboard boxes.

|      | Coating    | Colouring<br>agent                   | % Residual activity<br>after 4 weeks |         |
|------|------------|--------------------------------------|--------------------------------------|---------|
| 10   |            |                                      |                                      |         |
| A    | 7% MSP90   | 11.3%                                | 35%                                  | SD 4.5% |
| B    | 9% MSP90   | 11.3%<br>4% bisulfite                | 46%                                  | SD 6.7% |
| 15   |            |                                      |                                      |         |
| C    | 7% PEG4000 | 11.3%<br>4% bisulfite<br>5% Eudragit | 0.3%                                 | SD 0.1% |
| 20 D | 7% PEG4000 | 12.5%                                | 0.9%                                 | SD 0.4% |

The contents of the cardboard box is divided by  
means of a sample divider. 4 samples have been analyzed.

25

**EXAMPLE 9**

Preparation A-D: As example 7.

30

Preparation E: Preparation as preparation B,  
example 7, whereby 4% Na-bisulfite is substituted by 2%  
Na-ascorbate.

Storage conditions: Powerful acid bleach, 30°C,  
60/80% relative humidity, open glasses.

35

|    | Coating      | Colouring agent                      | % Residual activity after |         |
|----|--------------|--------------------------------------|---------------------------|---------|
|    |              |                                      | 1 1/2 week                | 3 weeks |
| 5  | A 7% MSP90   | 11.3%                                | 43-41                     | 23-25   |
|    | B 9% MSP90   | 11.3%<br>4% bisulfite                | 64-62                     | 36-37   |
| 10 | C 7% PEG4000 | 11.3%<br>4% bisulfite<br>5% Eudragit | 20-23                     | 9-8     |
|    | D 7% PEG4000 | 12.5%                                | 9-12                      | 4-4     |
| 15 | E 7% MSP90   | 12.5%<br>2% ascorbate                | 52-51                     | 28-32   |

## EXAMPLE 10

20

A granulate containing an amylolytic enzyme with the composition

25 15% fibrous cellulose, ARBOCEL BC 200  
4% kaolin, SPESWHITE ECC  
10% carbohydrate binder  
TERMAMYL dry matter/finely ground sodium sulphate ad 100%

30 was produced directly from a liquid fase enzyme as described in European patent publication No. 0 304 331 example 1, except that the enzyme in this example was TERMAMYL.

35 The granulate was dried in a fluid-bed to a water content below 1% and sifted between 300 µm and 900 µm.

The dry sifted granulate with an activity of 66 KNU/g was coated to generate the preparations A, B and C.

Preparation A: Fluid-bed coating with 5% Na-thiosulphate and 1.5% kaolin as described in example 4, preparation A, followed by a coating with 5.5% Grindtek MSP90 and 12.5% kaolin as described in example 1.

Preparation B: Coating with 10.5% Grindtek MSP90 and 25% kaolin as described in example 1.

Preparation C: Coating with 5.5% PEG4000 and 12.5% kaolin as described in example 1. This preparation is an example of prior art.

Storage ability of preparations according to example 10.

Storage conditions: Automatic Dish Washing detergent powder. 37°C, 70% relative humidity.

|    | Coating                            | Colouring agent | % Residual activity after |               |                |
|----|------------------------------------|-----------------|---------------------------|---------------|----------------|
|    |                                    |                 | <u>3 days</u>             | <u>7 days</u> | <u>14 days</u> |
| 20 |                                    |                 |                           |               |                |
|    | A 5.5% MSP90<br>(5% thio-sulphate) | 12.5%           | 85                        | 75            | 42             |
| 25 |                                    |                 |                           |               |                |
|    | B 10.5% MSP90                      | 25.0%           | 61                        | 45            | 24             |
|    | C 5.5% PEG4000                     | 12.5%           | 24                        | 20            | 6              |

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## CLAIMS

1. Granulate detergent enzyme product comprising a core  
5 of an enzyme-containing material and a coating thereon,  
wherein the coating comprises a coating agent, which is a  
mono- and/or diglyceride of a fatty acid, whereby the  
minimum content of monoglyceride in relation to the total  
content of mono- and diglyceride is 30% by weight,  
10 preferably 50% by weight, most preferably 75% by weight.

2. Product according to Claim 1, wherein the melting  
point of the coating agent is above 35°C, preferably above  
50°C.

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3. Product according to Claim 1 or 2, wherein more than  
90% of the enzyme granulate cores exhibit particle sizes  
between 2 and 3000 µm.

20 4. Product according to Claim 3, wherein more than 90%  
of the enzyme granulate cores exhibit particle sizes  
between 100 and 400 µm.

5. Product according to Claim 3, wherein more than 90%  
25 of the enzyme granulate cores exhibit particle sizes  
between 250 and 1200 µm.

6. Product according to Claims 1 - 5, wherein the  
weight of the coating is between 0.1 and 100% by weight of  
30 the core.

7. Product according to Claim 6, wherein the weight of  
the coating is between 1 and 30% by weight of the core,  
preferably between 2 and 20% by weight of the core.

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8. Product according to Claims 1 - 7, wherein the main fatty acid(s) of the coating agent is/are palmitic and/or stearic acid.

5 9. Product according to Claims 1 - 8, wherein the coating contains between 10 and 100% of the coating agent (on a dry substance basis).

10 10. Product according to Claims 1 - 9, wherein the coating also comprises a filler, which can be any salt, preferably  $\text{CaCO}_3$ ; talc, silica and/or  $\text{TiO}_2$ .

15 11. Product according to Claims 1 - 10, wherein the enzyme is one or more of a protease, an amylase, a lipase, a cellulase, and an oxidase.

12. Product according to Claims 1 - 11, wherein the particles of enzyme containing material are commercially available granulates.

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13. Product according to Claims 1 - 12, wherein the particles already possess or are given a coating containing or consisting of an antioxidant, preferably as an undercoat to the coating.

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14. Method for production of the product according to Claims 1 - 13, wherein the cores are introduced into a rotating mixer and heated to a temperature above  $35^\circ\text{C}$ , whereafter melted coating agent is added, and the product  
30 is removed from the rotating mixer when equilibrium is obtained.

15. Method for production of the product according to Claims 1 - 13, wherein the cores are suspended in melted  
35 coating agent and the thus formed mixture is introduced on

the surface of a fast spinning, horizontal wheel, whereafter the product is collected downstream the spinning wheel.

- 5 16. Method for production of the product according to Claims 1 - 13, wherein the cores are suspended in a solution of the coating agent in an organic solvent, whereafter the suspension is introduced into a fluid bed dryer and the product is collected.
- 10 17. Use of the granulate detergent enzyme product according to Claims 1 - 13 as a constituent of a detergent or a detergent component.
- 15 18. Use according to Claim 17, wherein the detergent or the detergent component appear as a slurry.
19. Use according to Claim 17, wherein the detergent or the detergent component appear as a particulate material.
- 20 20. Use according to Claim 17, wherein the detergent component is a bleaching agent.
21. Detergent or detergent component, containing as a  
25 constituent the product according to Claims 1 - 13.
22. Detergent or detergent component according to Claim 21, wherein the detergent or the detergent component appear as a slurry.
- 30 23. Detergent or detergent component according to Claim 21, wherein the detergent or the detergent component appear as a particulate material.
- 35 24. Detergent component according to Claim 23, wherein the detergent component contains a bleaching agent.

25. Detergent component according to Claim 24, wherein the bleaching agent is coated with a sustained release coating agent, preferably a sustained release coating agent containing montmorillonite.

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NOVO INDUSTRI A/S



# INTERNATIONAL SEARCH REPORT

International Application No PCT/DK89/00055

|   |  |                                     |
|---|--|-------------------------------------|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *  |  |                                     |
| According to International Patent Classification (IPC) or to both National Classification and IPC <sup>4</sup>  |  |                                     |
| C 11 D 3/386, 7/42  |  |                                     |
| <b>II. FIELDS SEARCHED</b>  |  |                                     |
| Minimum Documentation Searched <sup>7</sup>   |  |                                     |
| Classification System <sup>1</sup>  | Classification Symbols   |                                     |
| IPC 4   | C 11 D 3/386, 7/42; C 12 N 9/96, /98   |                                     |
| US C1   | 252:174.12, 174.13; 435:188; 195:63  |                                     |
| Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup>  |  |                                     |
| SE, NO, DK, FI classes as above.  |  |                                     |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>   |  |                                     |
| Category <sup>10</sup>  | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>   | Relevant to Claim No. <sup>13</sup> |
| X, Y  | EP, A2, 0 193 829 (MILES LABORATORIES, INC)<br>10 September 1986<br>See page 7, line 25 - page 8<br>line 13<br>& JP, 61209589<br>US, 4689297   | 1, 17                               |
| Y   | DK, A, 130 127 (UNILEVER NV)<br>23 December 1974<br>The whole document, especially<br>page 4, lines 11-13<br>& NL, 6814295<br>DE, 1801119<br>LU, 54618<br>FR, 1586260<br>CH, 505892<br>GB, 1242247<br>BE, 721881 | 1-2                                 |
| A   | EP, A2, 0 206 417 (THE PROCTER & GAMBLE<br>COMPANY)<br>30 December 1986<br>.../...   | 1-13, 17-24                         |
| <p>* Special categories of cited documents: <sup>14</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> |  |                                     |
| <b>IV. CERTIFICATION</b>  |  |                                     |
| Date of the Actual Completion of the International Search   | Date of Mailing of this International Search Report  |                                     |
| 1989-06-19  | 1989-06-19   |                                     |
| International Searching Authority   | Signature of Authorized Officer  |                                     |
| Swedish Patent Office   | Dagmar Järvman   |                                     |

| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) |  |                      |
|--|--|----------------------|
| Category *   | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No |
|  | The whole document, see especially claims 1 and 13-17, page 7, lines 22-28         |                      |